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MINERALOGY OF PLIOCENE TO PLEISTOCENE PELITIC SEDIMENTS OF THE GREAT HUNGARIAN PLAIN

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ABSTRACT

Mineralogical composition of pelitic sediments of the Great Hungarian Plain is reviewed in this paper. Published data and unpublished analyses made in the laboratories of the Geological Institute of Hungary a total of about 150 samples were collected. Determinations were made mainly by X-ray diffraction, the data were systematically corrected by comparison with the results of thermal analysis and partly chemical analysis. All data were revised and recalculated in a uniform system in order to obtain comparable results. In the bulk composition dominant clay minerals are smectite, illite/smectite, illite and chlorite. In the <2 μm fraction the same minerals occur, however, expanded phases are more dominant. Triple mixed-layer illite/smectite/chlorite and kaolinite of various degree of disorder may appear. Clay minerals are essentially detrital, derived from various areas of the surrounding Carpathians and Alps. Sub-basins may differ in degree of disorder and quantitative proportions of clay minerals and quantitative relations of other phases like calcite, dolomite, quartz and feldspars depending on relatively permanent source areas and transport directions. Smaller variations in the transport directions as shown by the micromineralogical composition are normally not reflected in the clay mineral record, neither climatic variations during the Pleistocene seem to have significant effect. In the South Tisza Basin and Maros Alluvial Fan well crystallised detrital phases prevail while in the Körös Basin more mature sedimentary material of lesser crystallinity, higher kaolinite and very low carbonate contents can be found. The clay, carbonate, feldspar and iron minerals deposited may have been modified by flow systems of ground water. In the upper flow regime comprising Pleistocene and Pliocene horizons of the South Tisza Basin and Maros Alluvial Fan dissolution of carbonate minerals and albite and ion exchange on clay minerals may proceed. In the stagnant ground waters filling the Pleistocene and Pliocene beds of the Körös Basin neoformation of pure smectite and kaolinite from dissolution of albite and dissolution of carbonates may be inferred from hydrogeochemical and mineralogical data. Amorphous iron hydroxides underwent crystallisation and reduction producing, in a downward sequence, amorphous "limonite", goethite and siderite. No diagenetic K-fixation and illitisation occurs in this level, however, some kind of palaeo-pedological illitisation may have occurred in those continental sediments. The first main step of burial diagenetic illitisation as well as of kerogen diagenesis starts in the lower groundwater regime which corresponds to the Upper Pannonian stratigraphic horizon, i. e. below the formations discussed in the present paper.

Key words: alluvial deposits, variegated clay, Great Hungarian Plain, Pliocene, Quaternary, clay minerals, rock-water interaction.

INTRODUCTION

The rocks filling the basin of the Great Hungarian Plain and other major sub-basins of the Pannonian Basin, the Dráva Basin and the Little Hungarian Plain, are mainly clastic detrital sediments, the composition of which is primarily determined by source rocks, conditions of transport and sedimentation (Rónai 1985, Jámbor 2001). The unusual thickness of the sedimentary column, deposited even in the youngest geological periods, in the Upper Pliocene and Quaternary, gives way to the secondary processes such as incipient burial diagenesis and interaction with the flowing groundwater.

In the classical works of the research team of Rónai (1972, 1985) and in subsequent studies, petrography was mainly restricted to the micromineralogical analysis (see e. g. Molnár, 1965, Thamó-Bozsó, 1997). Less attention was given to the rock-forming components, such as clay, carbonate and iron minerals. A brief summary of clay mineralogy of Quaternary sediments was made by the present author as part of a broader review of all Hungarian lithostratigraphic formations (Viczián, 1987).

In the present review the stratigraphical and regional geological summaries of Jámbor (1998, 2001) were chosen as geological background. Jámbor (1998) considered that the type of Hungarian Quaternary sediments is defined primarily by the geomorphological conditions of sedimentation and classified sediments as deposited in (I) flatland, (II) hilly and (III) mountainous areas (Fig. 1). Sediments of mountainous and hilly areas were reviewed recently by Viczián (2002). In the following we shall deal with the flatland areas trying to summarise our present knowledge on mineralogical composition of fine-grained sediments of basin areas.

Lithostratigraphic formations defined by the Stratigraphic Commission of Hungary (Császár, ed., 1997), will be grouped according to this major subdivision. In spite of the uncertainties inherent of the use of lithostratigraphic names in the Quaternary, such units were referred to in the present review in order to find a systematic frame for the discussion. Many Quaternary sequences are closely related to the underlying Pliocene formations, it is difficult to draw a sharp boundary between them. This is the reason why in most cases the discussion has been extended to the period preceding the Quaternary.

METHODS

Data on the composition of Quaternary clays are based mainly on results of X-ray diffraction analysis. In cases of old X-ray data made in the laboratory of the Hungarian Geological Institute the original evaluations of the X-ray records were revised by the present author during the preparation of the manuscript in 2001-2002. Such data are indicated in the text as "revised". When possible, only these revised data were used in the discussion in order to avoid sources of error due to variable authors and changing methods during the last decades. In addition to X-ray diffraction, the results of other analytical methods, especially those of thermal analysis will be considered.

RESULTS: MINERALOGY OF QUATERNARY SEDIMENTS OF SUB-BASINS OF THE PANNONIAN BASIN

Geological subdivision, basic data

Out of the three main flatland areas in Hungary the most mineralogical data are available from the Quaternary sediments of the *Great Hungarian Plain (Alföld).* The surface of Alföld is covered primarily by alluvial deposits, wind-blown sand and loess. The thickness of the Quaternary varies in wide ranges (see the map of Franyó, 1992 *in* Nádor et al., 2000) and may exceed 400-600 m in the deepest sub-basins. There are three major sub-basins in the Great Plain area (see Fig. 1): *Jászság Basin* in the north, *South Tisza Basin* along the Tisza river in the south and *Körös Basin* along the Körös river in the east (Rónai, 1985, pp. 69-71). The *Maros river alluvial fan* borders with the *Körös Basin* in the north and with the *South Tisza Basin* in the west. The sediments filling these sub-basins are developed mostly in a cyclic fluvial facies. These sequences were mostly revealed by the key bore holes of the Alföld Programme of the Hungarian Institute of Geology in the 1960-1970 years (Rónai, 1985). Important data were obtained also from other investigations, mostly from water and CH exploration drill holes. Cross sections of the sub-basins along the major bore holes are shown in Figs. 2, 3 and 4, including the basic mineralogy of the lithostratigraphic units.

There is a single bore hole in the *Dráva Basin, Görgeteg-1*, the thick

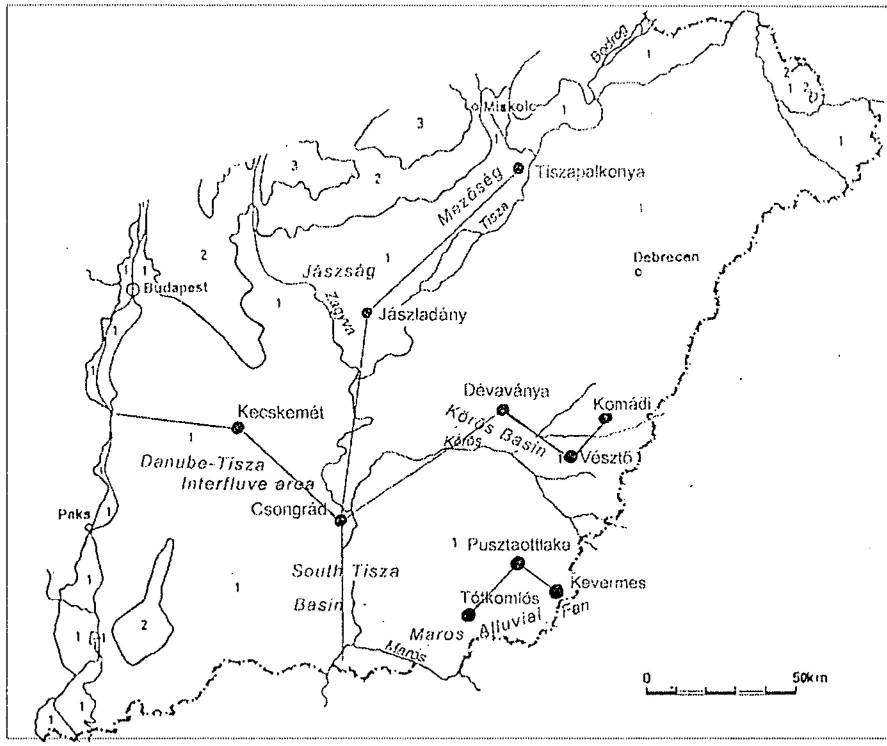

Fig. 1. Index map of the Great Hungarian Plain showing geographical local names mentioned in the paper. The lines of the geological cross sections shown in *Figs. 2-4* are indicated. The map shows the subdivision of the territory according to geomorphologic types of accumulation of Quaternary sediments (Jámbor, 1998, Fig. 4). Legend: 1. basin, 2. hilly, 3. mountainous areas

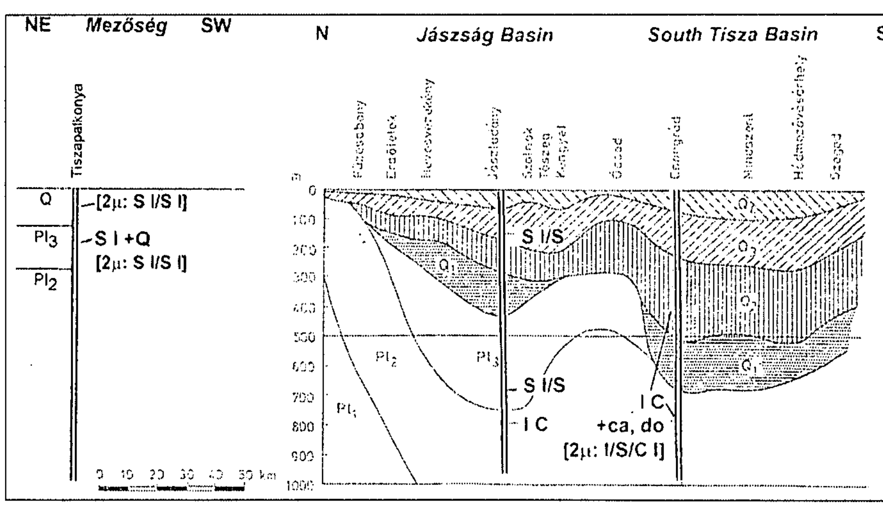

Fig. 2. Characteristic bulk mineral and clay mineral assemblages of Pliocene and Quaternary stratigraphic units of the Great Hungarian Plain along cross sections in north-east – south-west, and north – south direction. Geological cross section across the Jászság and South Tisza Basins according to Rónai (1986, Fig. 4). Geological data for the borehole Tiszapalkonya were taken from Tanács (1986). Abbreviations of the stratigraphic units: Q_1: Lowermost Pleistocene, Q_2: Lower Pleistocene, Q_3: Middle Pleistocene, Q_4: Upper Pleistocene, Q: Pleistocene (undivided), Pl_1: Lower Pannonian, Pl_2: Upper Pannonian, Pl_3: Uppermost Pliocene. Legend: Quantity of minerals in the cross sections: *capital letters:* frequent phases, >50 % of total clay minerals, *lower case letters:* less frequent phases. Minerals: S, s: smectite, I/S, i/s: mixed-layer illite/smectite, i/c: mixed-layer illite/chlorite, I/S/C: mixed-layer illite/smectite/chlorite, I, i: illite, K, k: kaolinite, k/s: mixed-layer kaolinite/smectite, C, c: chlorite, Q, q: quartz, kf: K-feldspar, pl: plagioclase, ca: calcite, do: dolomite, sid: siderite, goe: goethite. In brackets: [2μ: ...]: characteristic minerals in the <2 μm fraction.

Quaternary sequence of which has been studied for clay minerals in the 1990's. Unfortunately, the mineral composition is not yet published, only the values of the *Kübler index* are briefly mentioned by Koloszár et al. (2001). We have no clay mineral data so far from young deposits of the *Little Hungarian Plain*. Therefore the mineralogy of these sub-basins is not discussed in the present review.

Results of the X-ray analysis of bulk rock samples are included in Table 1, those of the clay fraction in Table 2. The compositional ranges given in Table 1 were established in the following manner: Quantitative data given in percent were rounded up to the nearest 5 percent. In the compilation of the tables a few extreme values were not considered.

Quaternary alluvial deposits of the Jászság Basin (Jászladány Clay, Nagyalföld Variegated Clay and Kerecsend Red Clay? Formations) and Mezőség (Jászladány Clay? and Nyékládháza Gravel Formations)

The thick Quaternary sequence of the *Jászság Basin* was recovered by the key borehole *Jászladány-1* of the Alföld Research Programme which crossed 430 m of a fluvial and flood plain sequence consisting of alternating clay and silt beds (Rónai, 1972, see Fig. 2). Today, in the stratigraphic system, this is called Jászladány Clay Formation. Quaternary is underlain by Upper Pliocene carbonate-poor variegated clays between 432 and 730 m (Nagyalföld Variegated Clay and Kerecsend Red Clay? Formations), which are sediments of shallow lakes and flood plains multiply redeposited in a dry and warm period. Below 730 m alternating sand, silt and clay layers represent the Upper Pannonian (Újfalu Sandstone Formation).

A great number of DTA analyses of this sequence were made by Székely in 1965. She has found only *illite* as clay mineral throughout the Quaternary and *illite+kaolinite* in the Pliocene. The first 4 X-ray analyses published from the Alföld area were made on samples from this bore hole by Rischák (1965, see Rónai, 1972, revised). *Smectite+illite/smectite* and less illite were found in a black peaty clay sample of Middle Pleistocene age at 155 m (Jászladány Clay Formation). Much *smectite+illite/smectite*, less illite and chlorite are in two Upper Pliocene samples, in a reddish brown clay sample at 684 m (Kerecsend Red Clay? Formation, see the X-ray pattern in Fig. 5) and in a grey silt sample at 688 m (Nagyalföld Variegated Clay? Formation). It was possible to estimate the proportion of smectite (S%) in the mixed-layer phase on the ethylene glycol treated patterns in all three samples: in falls into the interval 60-100 S% and there is a lesser amount between 0-40 S%. Rónai (1972, p. 54) considered reddish brown clays of Upper Pliocene age in the depth interval 670-685 m as "particularly important" being analogous with the red clays occurring under the loess beds in SE-Transdanubia and in the foothill area of Mátra and Bükk Mts. Indeed, high smectite contents are typical properties of the red clays both at *Jászladány* and in the localities on the northern margins of the Great Hungarian Plain (Kerecsend Red Clay Formation? see the review of Viczián, 2002). High smectite contents in Quaternary clays indicate probably the importance of the volcanic source rocks in the *Jászság Basin* and in the case of the red clays also the climatic conditions. Low carbonate contents are typical in Transdanubian red clays of the upper Tengelic Formation

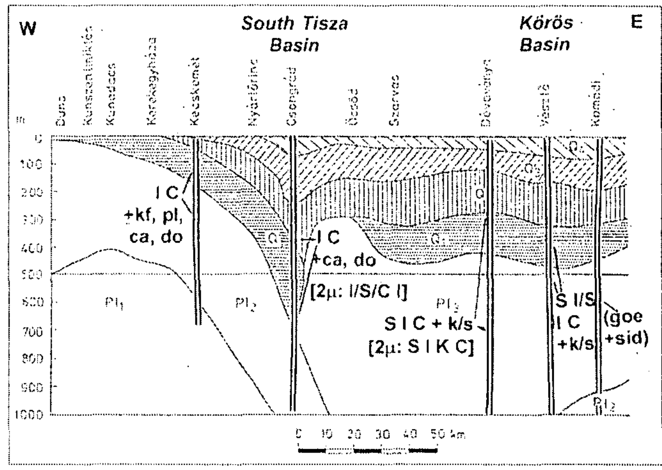

Fig. 3. Characteristic bulk mineral and clay mineral assemblages of Pliocene and Quaternary stratigraphic units of the Great Hungarian Plain along a cross sections in west - east direction. Geological data on the South Tisza and Körös Basins according to Rónai (1986, Fig. 5). For abbreviations of the stratigraphic units and legend of minerals see Fig. 2.

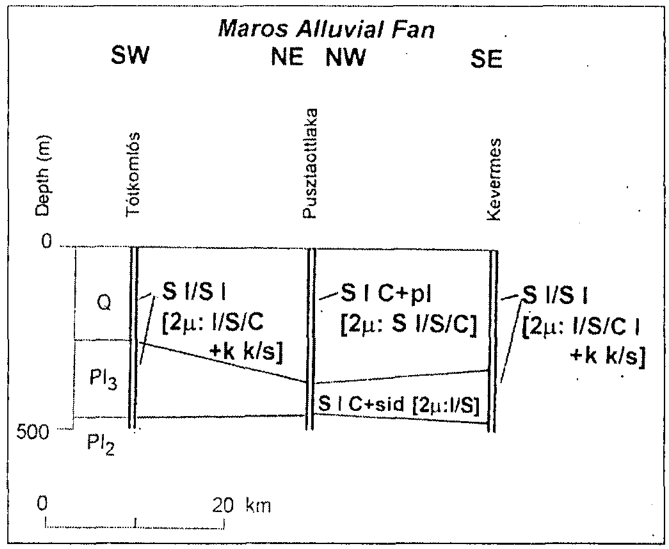

Fig. 4. Characteristic bulk mineral and clay mineral assemblages of Pliocene and Quaternary stratigraphic units across the Maros Alluvial Fan. The section was compiled using the geological data of Franyó (1983). For abbreviations of the stratigraphic units and legend of minerals see Fig. 2.

whereas at Visonta variable calcite contents in the red clay beds are the result of subsequent pedogenic processes (Horváth et al., 2001). In the Upper Pannonian (Újfalu Sandstone Formation) there is more carbonate, and clay minerals are represented by the detrital assemblage of *illite* and *chlorite*.

The borehole *Tiszapalkonya-1* is located in the *Mezőség* area, in NE continuation of the *Jászság Basin* (Fig. 2). The whole Quaternary sequence is here only 128,2 m thick (unpublished report by Tanács, 1986). Only the composition of the <2μ m fraction of 5 Quaternary clay samples was determined. Clays are thin intercalations in a generally coarse-grained sequence. Lithostratigraphic units were not identified, most probably they represent the Jászladány Clay and the Nyékládháza Gravel Formations.

Table 1. Mineral composition of bulk samples of Quaternary and Upper Pannonian formations of various sub-basins of the Great Hungarian Plain

Basin	Borehole	Formation	Age	No. of samples	smec. (* + Na-s)	i/s	illite	kaolinite (*k/s)	chlorite	quartz	K-feldspar	plagioclase	calc. (* +Mg-c)	dol. (* + Fe-d)	siderite	goethite	pyrite	q/fp ratio
JÁSZSÁG, MEZŐSÉG	*Jászladány-1*	Jászladány Clay	Q_1	1	35		15-20	0-5		35		10						3.5
		Kerecsend Red Clay(?)	Q_1	1	45		20		5-10	15-20			0-5	0-5	5			"?"
		Nagyalföld Variegated Clay(?)	Pa_2(Pl)	1	30		20		5-10	35		5						5.8
		Újfalu Sandstone	Pa_2(M)	1	5-10		25		15	15-20		5	15	10-15				3.6
	Tiszapalkonya-1	Nagyalföld Variegated Clay	Pa_2(Pl)	2	10	0-5	10-15	0-5	0-5	55-60		5						5.5-6.1
SOUTH-TISZA, DANUBE-TISZA INTER.	*Kecskemét-1*	Kecskemét Gravel	Q_1	5	0-5	0-5	10-30		5-20	20-50	5-15	5-20	5-15	5-15			tr.	1.1-3.6
		Újfalu Sandstone	Pa_2(M)	16														0.8-3.6
	Csongrád-1	Csongrád Sand	Q_1	9	5-15	0-5	20-30	0-5	10-20	20-25	0-5	5-10	5-15	5-15	tr.		tr.	1.2-4.5
		Újfalu Sandstone	Pa_2(M)	6														2.3-11.5
KÖRÖS	*Dévaványa-1*	Vésztő Variegated Clay	Q_1	6	10-20	0-10	20-40	0-10*	10-15	25-30	0-5	10	0-5		tr.	tr.		1.1-4.0
		Nagyalföld Variegated Clay	Pa_2(Pl)	13														1.2-4.6
	Vésztő-1	Vésztő Variegated Clay	Q_1	4	10	10	15-25	0-5*	5-10	30-50	0-5	5-10	0-5*	tr.		0-5	tr.	2.6-11.3
		Nagyalföld Variegated Clay	Pa_2(Pl)	11														5.3-8.3
MAROS ALLUVIAL FAN	*Pusztaottlaka-I/P*	Vésztő Variegated Clay	Q_1	14	5-15	0-10	15-30	0-5	5-15	20-40	0-5	10-25	0-5*	0-5			tr.	0.6-2.7
		Nagyalföld Variegated Clay	Pa_2(Pl)	12	5-15	0-10	15-30		5-15	20-40		5-10	0-15	0-5	0-10		tr.	2.3-4.8
	Kevermes-II/P	Vésztő Variegated Clay	Q1	18	5-30*	5-15	15-30	0-5	5-10	15-40	0-5	5-15	0-10*	0-10*	tr.			0.7-4.3
		Nagyalföld Variegated Clay	Pa2(Pl)	13	20-40*	5-15	20-35	0-5	5-10	10-20	0-5	0-15	0-5			0-5		1.1-7.5
	Tótkomlós-III/P	Vésztő Variegated Clay	Q1	15	20-35	5-10	15-20	0-5	5-10	20-35	0-5	5-10	0-15	0-5		tr.		1.6-7.0
		Nagyalföld Variegated Clay	Pa2(Pl)	28	15-35	5-20	15-20	0-5	5-10	20-35	0-5	5-10	0-10	0-5	0-5		0-5	3.1-7.3

Q1: Pleistocene, Pa2 (Pl): Upper Pannonian (Pliocene), Pa2 (M): Upper Pannonian (Miocene)
smec.: smectite, + Na-s: (Ca,Mg)- and Na-smectite, i/s: illite/smectite mixed-layer mineral, k/s: kaolinite/smectite mixed-layer mineral, calc.: calcite, + Mg-c: in some samples magnesian calcite, dol.: dolomite, + Fe-d: in some samples Fe-dolomite
tr.: traces
q/fp ratio: quartz/feldspar ratio

Table 2. Mineral composition of the <2 µm fraction of Quaternary and Upper Pannonian formations of various sub- basins of the Great Hungarian Plain

Basin	Borehole	Formation	Age	No. of samples	smectite+i/s (*: i/s/chl)	illite	kaolinite (*: k/s)	kaolinite/ chlorite relation	chlorite	S in i/s (%)
JÁSZSÁG, MEZÕSÉG	*Tiszapalkonya-1*	Pleistocene	Q_1	5	55-75	20-40	0-5*	>	0-5	20-100
		Nagyalföld Variegated Clay	Pa_2(Pl)	3	50-65	30-45	5-10		0-5	60-100
SOUTH-TISZA, DANUBE-TISZA INTERFLUVE	*Kecskemét-1°*	Kecskemét Gravel	Q_1	1	45	50	0-5	<	0-5	
		Újfalu Sandstone	Pa_2(M)	10	0-20	65-90	0-5		5-15	
	Csongrád-1 (>5µm)	Csongrád Sand	Q_1	9	35-60*	20-50	5-10	<	5-10	20-40; 60-100
		Újfalu Sandstone	Pa_2(M)	6						0-20; 60-100
	Csongrád-1 (>2µm)	Csongrád Sand	Q_1	9	55-70*	20-35	5-10	~	5-10	10-20; 40-100
		Újfalu Sandstone	Pa_2(M)	6						0-20; 40-100
KÖRÖS	*Dévaványa-1*	Vésztõ Variegated Clay	Q_1	6	30-50	30-40	10-20*	~	10-20	20-40; 100
		Nagyalföld Variegated Clay	Pa_2(Pl)	13						0-40; 60-100
MAROS ALLUVIAL FAN	*Pusztaottlaka-I/P*	Vésztõ Variegated Clay	Q_1	14	65-85*	10-25	5-10	~	5-10	70-90
		Nagyalföld Variegated Clay	Pa_2(Pl)	12	65-85					
	Kevermes-II/P	Vésztõ Variegated Clay	Q_1	6	60-75	20-35	5-10*		0-5	0-10; 40-100
		Nagyalföld Variegated Clay	Pa_2(Pl)	6	60-80*	15-30				
	Tótkomlós-III/P	Vésztõ Variegated Clay	Q_1	15	55-80*	10-30	5-10		0-10	60-100
		Nagyalföld Variegated Clay	Pa_2(Pl)	28	60-85*	5-30	5-15*		0-10	80-100

° Data not revised.

Q_1: Pleistocene, Pa_2 (Pl): Upper Pannonian (Pliocene), Pa_2 (M): Upper Pannonian (Miocene)

i/s: illite/smectite, i/s/chl: illite/smectite/chlorite, k/s: kaolinite/smectite mixed-layer minerals

S in i/s: proportion of smectite in illite/smectite (%, approximate estimates)

In cases when kaolinite and chlorite contents fall in the same range, the actual quantitative relations are shown by the signs <, > and ~

The Upper Pliocene Nagyalföld Formation underlies unconformably the Quaternary deposits (128,2-266,2 m), which is, in turn, underlain by the very thick Upper Pannonian Bükkalja Lignite Formation. This latter one is not discussed in the present paper. From the Nagyalföld Formation 2 bulk samples and 3 samples of the <2μ m fraction of clay beds were analysed. X-ray diffraction analysis was made by Viczián in 1986. In the bulk samples there are low carbonate contents. The dominant clay minerals are *smectite* and *illite* while kaolinite and chlorite are low. All clay minerals are opressed by the unusually high amounts of *quartz* which is probably due to the generally coarse-grained nature of the enclosing clastic sequence (Table 1). In the <2μ m fraction of both Quaternary and Nagyalföld Formations, *smectite, illite/smectite* and *illite* are the main components, only little kaolinite and chlorite are left in the fine fraction. There is more kaolinite than chlorite. Kaolinite is disordered in Lower Pleistocene (Table 2). Smectite proportions in the mixed-layers are very variable in the Nagyalföld Fm. (60-100 %) and even more in the Pleistocene (20-100%). The sudden drop in S % values corresponds to the erosional unconformity between Upper Pliocene Nagyalföld Fm. and Pleistocene.

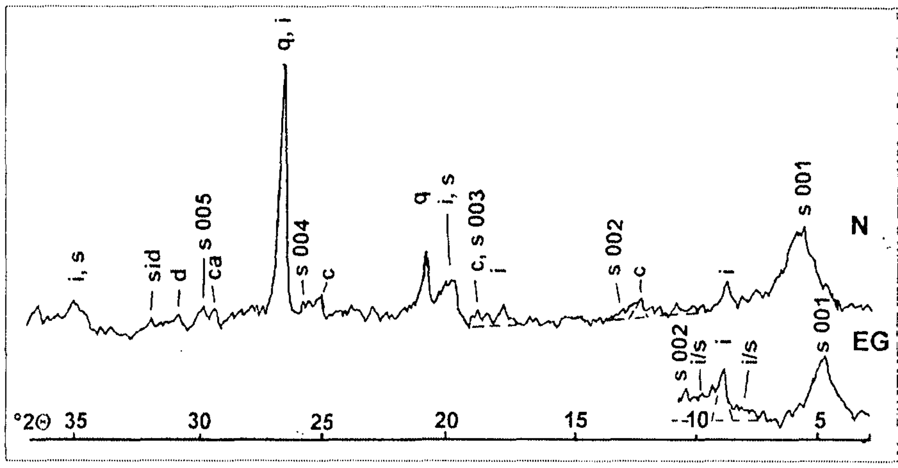

Fig. 5. X-ray diffraction patterns. Borehole Jászladány-1, 683.99-684.24 m, reddish brown clay, bulk sample, Kerecsend Red Clay (?) Formation, Upper Pliocene. Original analysis by Rischák (1965, revised), one of the first X-ray patterns made of the Quaternary deposits of Great Hungarian Plain. Conditions of the measurement: CuK_{α} radiation, N: untreated, EG: ethylene glycol treated sample, random powder specimens. Abbreviations of minerals: see Fig. 2.

Alluvial deposits of the South Tisza Basin (Csongrád Sand Formation) and of the Danube-Tisza Interfluve area (Kecskemét Gravel Formation)

The *South Tisza Basin* is a N-S stretching graben-like structure in which the deepest Quaternary basin of the Alföld area has developed. The thickness of Quaternary exceeds 600 m around the mouth of Körös river into Tisza (see Figs. 2 and 3). The basin is bordered from the west by an eastward dipping flank in the interfluve area of the present-day Danube and Tisza rivers. The thickness of Quaternary decreases westward from 650 m at the Tisza to less than 50 m at the Danube.

Lower and Middle Pleistocene sediments of the *Danube-Tisza Interfluve area* are mostly represented by sand-size (and sometimes gravel-size) fluvial deposits of the ancient Danube river called in the lithostratigraphic system Kecskemét Gravel Formation. There are a few XRD analyses showing the mineral composition of the intercalated clay and silt sediments from the key borehole *Kecskemét-1* (Rónai, 1985, see Fig. 3). The Quaternary sequence is 200 m thick. Quaternary is unconformably underlain by a thick sequence of mostly fine-grained Upper Pannonian fluvio-lacustrine sediments carried into the basin from NW direction (Újfalu, formerly Törtel Formation, see Juhász, 1992). Variegated clays of Pliocene age are missing here, pelitic sediments are of grey colour both in Quaternary and Upper Pannonian.

X-ray data of the bulk rock and <2μ m fraction composition of the whole sequence were determined by Viczián (1980, revised), published and interpreted in the C. Sc. Thesis of Gheith (1981b). The bulk samples in the entire sequence have a very uniform composition: major clay minerals are *illite* and *chlorite*, there are less smectite and illite/smectite, relatively much feldspar minerals: *K-feldspar* and *plagioclase* and carbonates: *calcite* and *dolomite* in nearly equal amounts. Kaolinite is practically absent. There is relatively much feldspar, the quartz/feldspar ratio varies typically between 1-2 in the sandstone and 2-3 in the clay (Table 1). This indicates immature sediments, the sandstone contains much lithic grains. The quantity of quartz – and correspondingly the amount of the rest of minerals – clearly varies with the dominant grain size, there is about 50 % quartz in sand and 20-30 % in silt and clay. Most carbonate minerals are detrital grains. According to Gheith (1981b) the <2μ m fraction is dominated by illite, while other clay minerals, smectite+illite/smectite, kaolinite and chlorite are little. Chlorite is normally more than kaolinite. This composition strikingly contrasts with that of any other Quaternary alluvial sediment from the Alföld. It was, however, not possible to revise these data during the writing this report because the original X-ray patterns are lost.

The overall mineral composition can be considered as typical of the sediment load of the Palaeo-Danube. Very similar compositions were reported from recent bottom sediments of the Danube in Austria (Kralik and Augustin-Gyurits, 1994) and at Bratislava (Konta, 1993). According to Konta, detrital *dolomite* is typical in the sediment load of Danube but absent in other rivers coming from the Bohemian Massif and from the Western Carpathians. In conclusion, Gheith (1981b, p. 179) stated that "the composition of sediments from *Kecskemét* can be directly related to the local erosion of sedimentary and metamorphic rocks and represent more reworked sediments".

The borehole *Csongrád-1* explored a similar coarse-grained fluvial sequence, but with a considerably thicker Quaternary (650 m), than in the well *Kecskemét-1* (see Figs. 2 and 3). Here the predominantly sandy succession (Csongrád Sand Formation) contains numerous gravel beds. The same types of sediments continue downwards in the Pliocene (Újfalu Formation, see Rónai, 1986, Figs. 4 and 5). The sediments were transported by river channels of the Palaeo-Danube from NW direction in Late Pliocene and Early Pleistocene times. Volcanogenic heavy minerals in Middle and Upper Pleistocene sands show more northern affinity similar to the deposits of the recent Tisza river (Gheith, 1982). No variegated clay occurs in this basin. Intercalated silt and clay layers were investigated by XRD. Bulk samples, the <2 μm fraction and - for experimental reasons - also the <5 μm fraction were studied (Viczián, 1979, published by Gheith, 1982, revised).

Similarly to the *Kecskemét-1* borehole, the bulk samples along the whole sequence have a very uniform composition: major clay minerals are *illite* and *chlorite*, there are less smectite and illite/smectite and occasionally kaolinite. K-feldspar and plagioclase are somewhat less abundant than at *Kecskemét*, there is less feldspar in the samples containing kaolinite. The quartz/feldspar ratio varies typically between 1 and 4 (Table 1), higher values indicate a certain degree of alteration. The sediments are rich in carbonates, both *calcite* and *dolomite* are present, microscopic observations have shown that the sediments are "enriched in detrital carbonate minerals" (Gheith, 1981b).

The <2μ m fraction contains much *smectite + illite/smectite* and discrete *illite*, while kaolinite and chlorite are invariably low throughout the whole Quaternary and Pliocene section. The 001/001 basal reflection of the expandable minerals ranges from 10 to 14 Å, the maximum is at about 12 Å indicating that the majority of the expanding phases is mixed-layer illite/smectite of high but variable smectite proportion (S %). S % values were determined on the glycolated specimens. Two broad maxima were found, one at about 0 to 20 % and another between 40 and 100 % smectite proportions. Glycolated and heated samples show that there is also

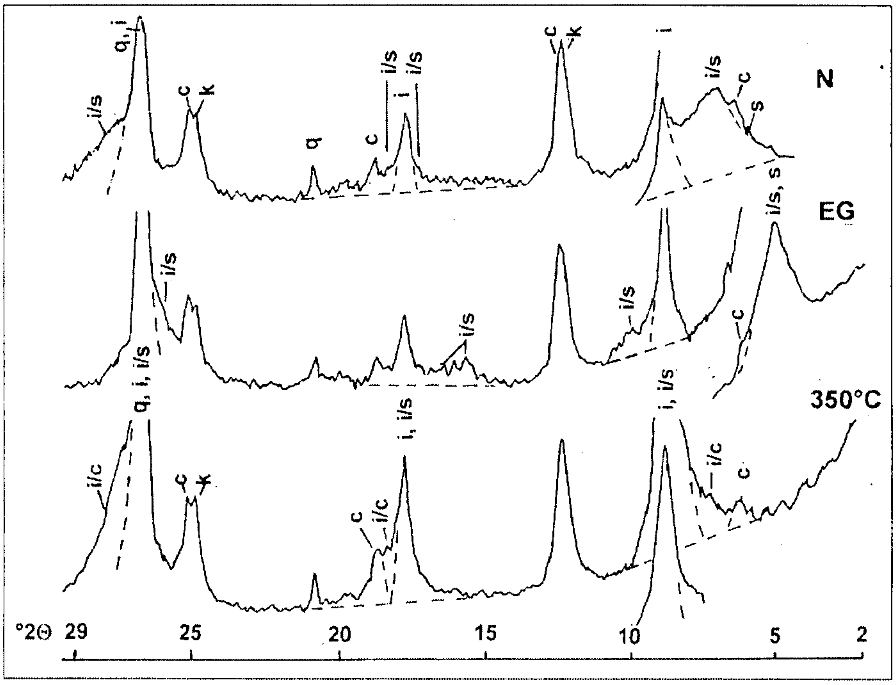

Fig. 6. X-ray diffraction patterns. Borehole Csongrád-1, core No. 10, 275.50-279.60 m, light grey calcareous siltstone, <2 μm fraction, Csongrád Sand Formation, Lower Pleistocene. Original analysis by Viczián (1979, revised). Conditions of the measurement: CuK_{α} radiation, N: untreated, EG: ethylene glycol treated sample, 350 °C: heated at 350 °C for 2 hours, oriented specimens by the smear-on-glass method. Abbreviations of minerals: see Fig. 2.

smectite/chlorite interstratification. Other minerals in the <2μ m fraction have normal sharp basal reflections (Fig. 6). The composition of the <5μ m fraction does not differ from the <2μ m fraction except that it contains slightly more illite and chlorite and slightly less kaolinite and smectite+illite/smectite. Chlorite is nearly equal to kaolinite in the <2μ m fraction and more than kaolinite in the <5μ m fraction, showing that kaolinite enriches in the finest grain fraction.

Usually these types of mixed-layer illite/smectite minerals are interpreted by pedogenic origin. Samples interpreted by micromineralogic analysis as being inherited from volcanic areas, do not display any systematic difference in the clay mineral composition, compared to the terrigeneous sediments of the Palaeo-Danube.

Alluvial fan of the Maros river (Vésztő and Nagyalföld Variegated Clay Formations)

The *Maros river alluvial fan* occupies the SE part of the Great Hungarian Plain. The facies of Quaternary and of underlying Upper Pliocene is variegated clay (Vésztő and Nagyalföld Formations, respectively), similarly to the *Körös Basin,* however, here the thickness of the formations is lower and the facies is more sandy. The samples taken from the fine-grained varieties of sediments were investigated in three water exploratory wells (Fig. 4).

In the well *Pusztaottlaka-I/P* the thickness of the Quaternary is 369 m, from here until the bottom of the well at 500 m, there are beds of Upper Pliocene (369-448 m) and Upper Pannonian (below 448 m) age (Franyó, 1983). 26 clayey and sandy siltstone samples were taken. The colour is partly grey, partly grey with yellowish brown spots. X-ray diffraction analyses on the bulk samples were made by Viczián (1979, unpublished data). Clay minerals are *smectite, illite/smectite, illite* and *chlorite.* Kaolinite is normally absent, however, there is an interval in the middle of Pleistocene where there is systematically about 5 % kaolinite. In this bore hole the value of the cation exchange capacity of the bulk samples was determined, 7-10 mol.10^{-3}/100 g (=15-20 meqv./100 g) which mostly depends on the smectite+ illite/smectite complex. Exchangeable cations are about ½ Ca, ¼ Mg, ¼ Na and little K.

Other minerals display systematic differences between Quaternary and Pliocene: quartz varies between 20-40 %, determining the quantity of the rest of phases. There is about 5 % K-feldspar in the Quaternary and missing in Pliocene, similarly, *plagioclase* contents are higher in Quaternary than in Pliocene. The reason of this distribution is perhaps stronger feldspar weathering in Pliocene. The dominant carbonate is calcite. Quaternary bulk samples are carbonate-poor (calcite 0-5 %, sometimes magnesian calcite, but the concretions consist of pure calcite). Pliocene samples are richer in *calcite* and *siderite*.

Data relating the <2 μm fraction were published by Viczián (1982). Contrary to the typical differences in the bulk composition, the proportion of clay minerals is practically the same throughout the section: the only dominant phase is *smectite+illite/smectite*, while illite, kaolinite and chlorite are present in low but nearly constant amounts. The smectite proportion of the expanding phases varies between 70 and 90 %. One systematic variation seems to be clear: Quaternary sediments contain *chloritic interlayers* in the mixed-layer structure while Pliocene mixed-layers are of the *illite/smectite* composition only. The overall character of the clay fraction resembles more the Danube river sediments of the *South Tisza Basin* than those of the *Körös* and *Jászság Basins*.

Another borehole investigated in detail in the course of the same water exploration project was *Kevermes II/P*. According to Franyó (1983), the thickness of the Quaternary is 320 m, there are beds of Upper Pliocene (320-489 m) and Upper Pannonian (below 489 m, until the bottom of the well at 500 m). A total of 31 samples were taken from the Quaternary and Pliocene interval. The rocks are alternating variegated siltstone indicating palaeo-weathering and humic clay of swamp horizons. X-ray diffraction analyses on the bulk samples were made by Rischák (1980, revised), thermal analysis by Földvári (1980). The dominant clay minerals are *smectite, illite/smectite* and *illite*, chlorite is less abundant. There is more smectite and illite in the Pliocene than in the Quaternary. A few per cent of kaolinite is present in most samples, slightly less frequently in the Quaternary. A peculiarity of the smectite is in almost every sample, that the 001 basal reflection splits into two maxima, one at about 12.5 Å and a stronger one at about 15 Å. This can be interpreted by the separation of *Na-* and *(Ca,Mg)-smectites*. Illite and chlorite are generally well crystallised, with sharp basal reflections. The highest quartz contents were found in sands of riverbed facies. Quartz and plagioclase are more abundant in the Quaternary than in the Pliocene, probably because slight differences in the grain size of the samples (more silt in the Quaternary and more clay in the Pliocene). A few percent of K-feldspar is present invariably in most Quaternary and Pliocene samples. The sediments are poor in carbonate minerals, the total carbonate contents are normally below 10 %, consisting mainly of calcite and less abundantly of dolomite. Magnesian calcite occurs throughout the whole Pleistocene but is missing in Upper Pliocene. Carbonate occurs in the sediments as nodules, spots, fill of fine network of veins and Mollusc shells. A carbonate nodule analysed consists of pure calcite.

In the <2 μm fraction the dominant clay minerals are *smectite, illite/smectite* and *illite*, kaolinite and chlorite are less abundant (originally analysed by Rischák, 1980, revised). The quantity relations are nearly the same as in the well *Pusztaottlaka-I/P*, here illite is slightly higher and chlorite somewhat lower. Kaolinite exceeds chlorite. There is practically no difference between the composition of the Quaternary and Pliocene samples. Smectite proportions in the *illite/smectites* vary in broad ranges, but normally are high, up to 100 %. The mixed-layer *illite/smectite* contains *chloritic interlayering*, as deduced from incomplete collapse of the basal reflection to 10 Å upon heating to 490 °C. This is true in the Pliocene samples, unfortunately, it was not determined in the Quaternary, because no heated specimens were made. Kaolinite is typically disordered, transitional to *mixed-layer kaolinite/smectite*. Typical weathering products are goethite in the Quaternary and anatase in the Pliocene, as minor amounts in the <2 μm fraction.

The third borehole in the *Maros alluvial fan* area was *Tótkomlós-III/P*. Geological and stratigraphic relations are nearly identical with those of the two previous wells (Quaternary: 0-248 m, Upper Pliocene: 248-480 m, Upper Pannonian below 480 m, Franyó, 1983).

X-ray analyses of the *Tótkomlós-III/P* samples were carried out by Rischák (1981, revised), thermal analysis was made by Rimanóczy (1981). Unfortunately, neither these data were published. The silicate phases of the bulk composition show basically the same quantitative relations as in *Pusztaottlaka-I/P*, however, differences between the Quaternary and Upper Pliocene are not so clear. As compared with *Pusztaottlaka-I/P*, there is somewhat more *smectite* and *illite/smectite* and less illite, chlorite and plagioclase in the *Tótkomlós-III/P* samples. Like in other occurrences of the Maros Alluvial Fan area, calcite, dolomite and siderite contents are low or zero both in Quaternary and in Upper Pliocene.

In the <2 μm fraction the type and quantity of the clay minerals is essentially the same, as in any other borehole of the Great Hungarian Plain, however, slight differences can be observed which are typical to the Maros river alluvial fan: *smectite+illite/smectite* are somewhat higher and *illite* lower than in other basins. Kaolinite is clearly higher than chlorite and there is *kaolinite/smectite mixed-layering* as indicated on broadening of the 001 basal reflection of kaolinite towards higher d-values. This kaolinite/smectite mixed-layering is more pronounced in the Pliocene than in the Quaternary. The smectite proportion in the illite/smectite varies in broad ranges, practically between 0 and 100 %, but it is most frequently in the range near 100 %. Illite/smectite seems to contain chloritic interlayers. This is typical invariably along the whole section. The general character of the clay fraction indicates even more "weathered" detrital sedimentary material, than at *Pusztaottlaka-I/P*, resembling more to *Kevermes-II/P*.

Alluvial deposits of the Körös Basin (Vésztő and Nagyalföld Variegated Clay Formations)

The *Körös Basin* represents a sub-basin in the *SE Alföld* area where especially thick Quaternary sequences were revealed. The dominant rock types are siltstone and clay interrupted by layers of sandy riverbed sediments (Vésztő Variegated Clay Formation). The formation continuously develops from similar formations deposited in the Upper

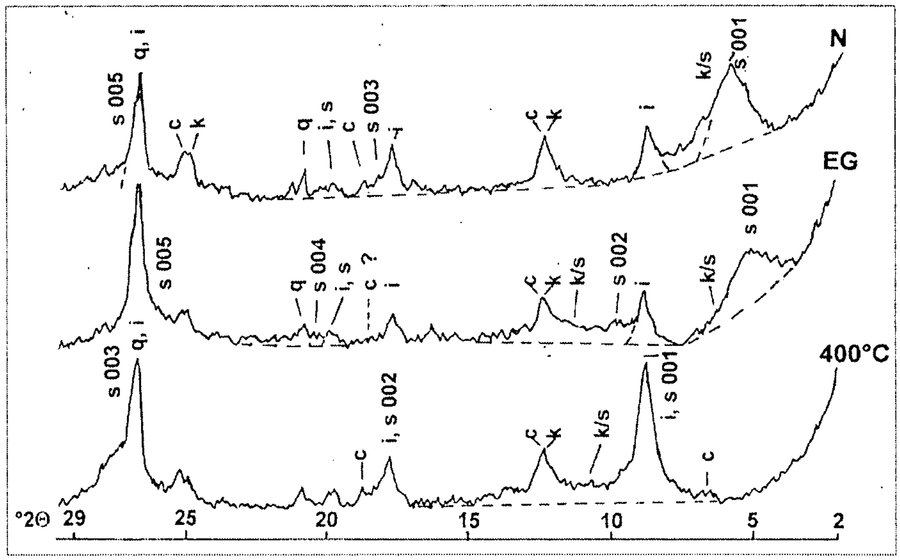

Fig. 7. X-ray diffraction patterns. Borehole Dévaványa-1, 172.9-181.0 m, variegated clayey silt, <2 µm fraction, Vésztő Variegated Clay Formation, Pleistocene. Original analysis by Szemethy (1978, revised). *"Weathered"* type bulk sample. Conditions of the measurement: see *Fig. 6,* 400 °C: heated at 400 °C for 2 hours. Abbreviations of minerals: see Fig. 2.

Pliocene period (Nagyalföld Variegated Clay Formation). The Upper Pliocene beds differ from the Quaternary ones only by their more lacustrine and marshy and less fluviatile character (Fig. 3).

The core material obtained from these formations from the borehole *Dévaványa-1* was object of detailed petrographic analysis by Gheith (1981a). Silt and clay samples were taken in 50-100 m intervals of the fine grained portions of the 1100 m thick sequence (Quaternary: 0-416 m). The XRD analysis of the bulk rock and of the <2 µm fraction was carried out by Szemethy (1978, revised) in the laboratory of the Geological Institute of Hungary. In the composition of the bulk samples the clay minerals *smectite*, *illite*, and *chlorite*, in lesser amounts mixed-layer illite/smectite and kaolinite occur. There are great differences between two types of mineral associations. In the *"weathered"* type samples the basal reflections are broad and uncertain, the quantity of smectite+illite/smectite is nearly equal to illite, there is a few percent of disordered kaolinite, the 001 basal reflection of kaolinite is asymmetrically broadened towards higher d values indicating *kaolinite/smectite interstratification.* There is another type which may be called *"fresh",* in which basal reflections are sharp, well crystallised *illite* and *chlorite* are the dominant phases, the quantity of expanded phases is low and there is no kaolinite. There is a third type in the lowermost portion of the Upper Pliocene in which smectite disappears and well crystallised kaolinite becomes more abundant. Among the other minerals of detrital origin quartz and plagioclase are constantly present while K-feldspar occurs only sporadically. Contrary to the sediments of Palaeo-Danube in the *Kecskemét* and *Csongrád* area, all rock types are poor in carbonate, only little calcite may be found in some cases.

In the <2 µm fraction the same clay minerals were found as in the bulk rock, however, *smectite* becomes the dominant phase and kaolinite appears in nearly equal amounts as chlorite, similarly, as in the <2 µm fraction of *Csongrád-1.* In this borehole both minerals are relatively high, compared to other localities (Fig. 7). Slight decrease of smectite and increase of kaolinite can be observed toward the bottom of the sequence (see Gheith, 1981a, Fig. 6). The maximum of the 001 basal reflection of *smectite*+illite/smectite is in this bore hole at about 14 Å. Another type of illite/smectite, present in lesser amounts, has basal reflection in the range 10-14 Å. This is a difference e.g. from the clay fraction of the samples of other bore holes of the Great Plain where the dominant basal spacing is almost invariably near 12 Å. As determined in the ethylene glycol treated samples, there are two ranges of composition of the smectite+illite/smectite expandable complex: one near 100 % smectite proportion and another one in the range of 20-40 % smectite proportion. Pliocene samples are slightly less expandable than Quaternary ones. *Kaolinite is disordered* and indicates *mixed-layering with smectite*, especially in the samples classified as "weathered" according to the bulk rock analysis (Fig. 7). Another difference from the *Csongrád-1* samples is the absence of chlorite/smectite interstratification.

In general, one can agree with Gheith (1981b, p. 179) who characterised *Dévaványa* sediments as "more mature which were deposited during quiet, more stagnant water conditions than those in *Csongrád* and *Kecskemét*".

Very similar figures were obtained for the bulk mineral composition of the 1200 m thick Upper Pliocene to Quaternary sequence of another key borehole, *Vésztő-1* (Quaternary: 0-482 m): smectite, illite/smectite, illite, kaolinite, chlorite, quartz, plagioclase and very little K-feldspar, calcite, dolomite, goethite and pyrite (traces in some cases). Quartz varies in broad ranges, between 30-50(-70) %, depending mainly on variations of grain size. This sequence seems to contain almost exclusively only the *"weathered"* type of the clay mineral suite which is reflected in the nearly equal ratio of smectite+illite/smectite to illite. No systematic variation in the quantity of most detrital minerals with depth or stratigraphic position can be observed, except variations due to grain size in the range of clay to fine sandy siltstone. The clays are almost carbonate-free, however, calcite is somewhat higher and contains 2-6 mol % Mg(+Fe?) in some Upper Pliocene samples. The unpublished XRD analyses were made by Viczián (1979, revised). The <2 µm fraction was not analysed.

DISCUSSION

Considerations on relation of clay mineralogy to palaeoclimatic conditions and source areas in the Körös Basin

It was attempted to find correlation between the mineralogy and *palaeoclimatic conditions* of deposition in the *Körös Basin*. The mineralogical data were compared with the results of palynological studies (Miháltz-Faragó, 1982). Miháltz-Faragó divided the Quaternary sections into 11 climatic zones which she identified with the Alpine glacial and interglacial periods. Her subdivision was accepted and highly estimated in the review paper by Jámbor (1998). The samples studied for clay minerals coincide with both warm and cold climatic conditions according to the pollen studies. However, no systematic variation of the mineralogy with the climate could be demonstrated except probably that some calcite is typical only in the colder stages while the warmer stage samples are carbonate-free.

An alternative view of the palaeoclimatic conditions during the deposition of the Quaternary sequences in the two bore holes was proposed recently by Nádor et al. (2000). Based on detailed sequence stratigraphic analysis, micromineralogical and palaeontological data and measurements of magnetic susceptibility, they recognised the existence of higher periodicity (100 and 40 Ky) Milankovitch cycles in the time interval of the Quaternary in the *Körös Basin*. According to this new model, sandy beds coincide well with maxima of magnetic susceptibility and in most cases with warm climatic periods. On the other hand, fine-grained beds may have different palaeo-environmental interpretation depending on the prevailing climatic conditions. In cold periods, due to low discharge, only fine-grained dispersed sediments reached the central parts of the basin and silts may have been deposited in the river bed facies while only fine clays reached the flood plains. On the other hand, in warm periods, due to higher discharge, the rivers deposited sand in the river bed and silt on the flood plain. By the finest resolution, however, in a dm to m scale of bed thickness the development of fine grained beds depends primarily on autocyclic shift of river bed and the effect of climatic variations is shown much more in the higher, approximately ten metres scale of the smoothed curve of grain size variation.

Unfortunately, the sampling density is not sufficient to check the possible compositional variations during an autocyclic or climatic cycle, on the basis of mineralogical data available at present. The present considerations are based on a very limited number of samples of Quaternary age, 6 from the *Dévaványa-1* and 4 from the *Vésztő-1* borehole.

It can be expected that the quartz/feldspar ratio or kaolinite contents may vary also in fine-grained rocks depending on the weathering conditions on the source area. The XRD data on quartz/feldspar ratios of fine-grained samples vary in the range 1 to 11 (Table 1). The most frequent values are at *Vésztő* 5 to 6 and at *Dévaványa* 2 to 4, i. e. the *q/fp ratio* of XRD analyses varies in the same range and probably in the same sense as the quartz/(feldspar+rock fragments) ratio in sandstones of the *Vésztő-1* borehole as determined by micromineralogical observations (Nádor et al. 2000). In the same time the palaeoclimatic interpretation may be discouraged by the fact that the same magnitude and range of variation of the quartz/feldspar ratio may be observed in the Quaternary as in the Upper Pliocene parts of the sections when a more balanced and less variable climate prevailed. The conclusion is much more plausible that for a long period of time a more mature material was deposited at *Vésztő-1* than at *Dévaványa-1*, independently of eventual climatic fluctuations during deposition.

Another discouraging aspect is the high degree of homogeneity in the mineralogical record in the <2 μm fraction throughout the whole sections of the two boreholes (Fig. 3). Even kaolinite contents are remarkably constant in the *Dévaványa-1* borehole, irrespective of eventual climatic variations. The remarkable fact that detrital clay mineral patterns may be *highly independent on palaeoclimatic conditions* was observed recently e. g. in the Mesozoic of England (Jeans et al., 2001). Similarly, Alcalá-García et al. (2001) have found that clay mineralogy of detrital sediments is more dependent on geodynamic factors than on palaeoclimate or facies of deposition. What is promising, however, it is the difference found between the "weathered" and "fresh" types of clay mineral assemblages in the Körös Basin Quaternary. Systematic comparison with other palaeoclimatic indicators would be necessary to check the correlation with these types of clay assemblages.

Similarly to the climatic variations, not much of the eventual variations of *the source areas* is reflected in the clay mineral record and bulk composition of the fine-grained sediments. Minerals of the *Dévaványa-1* borehole were interpreted by Gheith (1981a,b) as detrital depending on the source area, illite being derived from weathering of metamorphic rocks and smectite from volcanic rocks. This latter might be probably true for the major part of smectites because volcanogenic smectites should be discrete smectite phases and, indeed, 100 % smectite proportions are here the most common expandable types. There is, however, no much correlation with the eventual change of the source areas.

According to micromineralogical analysis, the source area of the *Körös Basin* sediments was generally the *Apuseni Mts.* from which the sediments were transported alternatively from NE-E and SE directions. Heavy minerals indicate predominantly metamorphic and redeposited Tertiary sedimentary rocks. In addition to these sources northern volcanic areas contributed material mostly in later periods of Quaternary at *Dévaványa* (Thamó-Bozsó and Kercsmár, 2000). The composition of the pelitic rocks does not reflect these variable source areas and *remains uniform* throughout the section.

The essential uniformity of the detrital material derived from the source areas was shown also by *isotope geochemical* studies. According to the study of the $^{87}Sr/^{86}Sr$ isotope ratio of the formation waters Varsányi (2000) concluded that in the Körös Basin this ratio is systematically different from the ratio observed in the Danube-Tisza Interfluve area and South Tisza Basin, reflecting different source areas of the sediments. Sediments of the Körös Basin have lower $^{87}Sr/^{86}Sr$ isotope ratios and, consequently, are derived from younger formations than those coming from the catchment area of the Danube river. These ratios and the corresponding source areas, however, remained essentially unchanged over the long time period from Late Miocene to Pleistocene.

The reason of this uniformity lies probably in the more averaged nature and slow speed of the development of the weathering crust which is one of the main sources of the pelitic material in the areas of denudation. Judging from the composition of the basin-filling material, the mineralogy of this weathering crust in the *Apuseni Mts.* may be similar to that of the Tengelic Formation in the Transdanubian area. Another source of the basin filling may be the redeposition of various Tertiary sedimentary rocks around the *Apuseni Mts.* which themselves may have rather uniform clay mineral composition. This can be identified partly with a frequently occurring chlorite-rich heavy mineral assemblage. The provenance of this assemblage was uncertain in the interpretation of the micromineralogical data but it was pointed out that Pannonian sediments commonly have similar chlorite-rich heavy mineral composition (Thamó-Bozsó and Kercsmár, 2000).

Similar observations were made by comparing Alpine source areas with Tertiary sediments in the South German Molasse Basin (Viczián, 1984), where a more uniform clay mineral assemblage was observed than it might be expected from heavy mineral studies. It was shown, however, that probably more accurate measurements of structural parameters of micas may reveal differences in different metamorphic source rocks.

Diagenesis of iron minerals in the variegated sediments of the Great Hungarian Plain

Vary-coloured sediments of the Great Hungarian Plain with typical yellowish rusty spots give good insight into the repartition and transformation of iron minerals after deposition.

In deeper zones of the borehole *Csongrád-1* traces of siderite and pyrite show the reduced state of iron. Gheith (1982) observed that in higher levels most of the Quaternary fine-grained "samples have stained patches of *limonite*". This, however, does not appear in the X-ray record.

The typical rusty yellow and reddish spots correspond to traces of goethite in borehole *Dévaványa-1* in the *Körös Basin* area. The high ferric/ferrous iron proportions (2:1 to 5:1) in the chemical analyses show the oxidised state of the pelitic sediments (see Fig. 4 of Gheith, 1981a). It is more clearly seen in the borehole *Vésztő-1*, than in *Dévaványa*, that rusty spots may be attributed to the iron mineral *goethite*, especially in the Upper Pliocene part of the section. In the Upper Pliocene also iron-containing calcites may occur.

Variegated clays from the *Komádi-1* borehole were investigated by Rischák (1984). The samples were taken from the deeper part of the sequence (Upper Pliocene Nagyalföld Formation, see Fig. 3). The studies were focused to the genesis of the red spots. In the red parts of the samples the iron minerals *goethite, lepidocrocite* and *siderite* were identified by XRD, thermal (Rimanóczy, 1981, see Rischák, 1984, Table 2) and chemical analysis. Ferric iron is derived of *pyrite* by the oxidation of sulphide to sulphuric acid, migration of ferrous ions to the spots in a local scale, precipitation of ferrous carbonate and finally oxidation and precipitation in form of ferric hydroxides. Bulk mineral composition remains unchanged during this process and is practically identical with that of the two other boreholes studied in the *Körös Basin*.

In the water exploratory well *Pusztaottlaka-I/P* in the *Maros alluvial fan* area Upper Pliocene (Nagyalföld Fm.) samples may contain much *siderite* (0-10 %, in some cases up to 25 %, according to the quantitative determinations of Földvári by thermal method). Siderite and traces of pyrite indicate reductive marshy environment. No crystalline goethite was indicated by the XRD, however, "limonite" was identified in the deeper Quaternary and higher Pliocene samples by thermal analysis. This indicates that *poorly crystallised iron(III) hydroxide* of the higher zones is replaced by reduced iron carbonate in the deeper horizons of the Pliocene Nagyalföld Fm.

On the other hand, in the well *Kevermes-II/P* iron carbonates, such as Fe-containing dolomites and traces of siderite occur in the upper 120 m zone of Quaternary. Crystalline goethite in the bulk samples appears only in the Upper Pliocene, however, in the <2 μm fraction it can be traced also in the Quaternary.

The relation among iron minerals in the water exploratory well *Tótkomlós-III/P* is the same as in *Pusztaottlaka-I/P*: Almost no crystalline goethite was indicated by XRD but "limonite" was frequently identified by thermal analysis in the Quaternary sediments, indicating that *iron hydroxides* are *partly amorphous* or poorly crystallised. *Siderite* occurs sporadically in the Quaternary but it is a more common component in the Upper Pliocene. Siderite may be identified both by thermal analysis (0-15 %) and X-rays (in one sample: 10 %, commonly 0-5 %). In organic-rich dark sediments also *pyrite* occurs.

The reduction of iron (III) minerals and the simultaneous desorption of arsenic compounds (possibly arsenite anions) from the surface of iron (III) hydroxides is closely related to the formation of *arsenic groundwater* in the area of the *Maros alluvial fan* (Bartha et al., 1999, 2000) and other areas of the *Great Hungarian Plain* (Csalagovits, 1999).

Possible illitisation in palaeosols

Tanács and Viczián (1995) observed increase of the variability of the smectite proportions in the mixed-layer illite/smectites of fluvial and continental sediments and palaeosols in the upper part of the Upper Pannonian (Pliocene) and in the Pleistocene, as compared to underlying lacustrine or marine Pannonian deposits. As it was shown in the present review, smectite ratios may vary in the same sample within broad ranges, sometimes between 20 and 100 %.

Tanács and Viczián (1995) considered to be not probable that this high variability of the smectite ratios in the highest levels is related to burial diagenesis. Most probably it is due to *palaeo-pedological processes of illitisation* during subaerial exposure of the sediments immediately after deposition. Details of these processes are, however, not yet clear.

Diagenesis of clay minerals, water-rock interaction

Thermal data were published by Rónai (1985, Fig. 334, p. 367) in a geological cross section of the *Körös Basin*, crossing the wells *Szarvas, Dévaványa* and *Vésztő*. The 40 °C isotherm runs in the depth interval of 400-500 m and the 60 °C isotherm in the depth interval of 800-1000 m. On the other hand, data from the whole Pannonian Basin show that the burial diagenesis of illite/smectites starts at temperatures somewhat higher than 60 °C (Viczián, 1994). This means that diagenesis of the expanded clay minerals caused by thermal effects cannot be expected in the Quaternary, even in the deepest basins.

In this zone the main controlling factor of diagenesis is the *interaction of the sediments with the flowing groundwater.* The chemical reactions between water and solid phases modify the original composition of both the waters and of the enclosing sediments. In the following it will be attempted to compare data related to groundwater and solid phases, and to find evidence in the mineralogical analyses supporting the results of hydrogeochemical calculations.

There are hydrogeochemical studies on interaction of formation waters with young sediments in various parts of the southern Great Hungarian Plain (see review papers by Varsányi and Ó.Kovács, 1994 and Varsányi, 2000, 2001). Unfortunately, there are no similar detailed studies yet available from other parts of the Pannonian Basin. Based on earlier studies of Erdélyi (1979), Varsányi et al. (1997) and Varsányi (2000) came to the important conclusion, that water *flow systems* developed *above the Lower/Upper Pannonian* lithostratigraphic boundary. *Under this boundary* there is a completely different water regime with practically *stagnant, concentrated* $NaCl$-$NaHCO_3$ type waters.

Above the Lower/Upper Pannonian boundary two main water flow regimes were separated. The lower one, a *regional-scale water flow regime* in the Upper Pannonian (Upper Miocene, "Pontian M_3Po" of Varsányi, 2000, 2001) is less well known from geochemical point of view. Water-rock interaction was especially well studied in the *upper intermediate-scale water flow regimes* that comprise the Upper Pliocene and Pleistocene sediments of the southern Great Hungarian Plain. As shown in Tables 1 and 2 and in Figs. 2, 3 and 4, the majority of the samples reviewed in the present paper belongs to this *upper water flow regime.*

The *Danube-Tisza Interfluve Area* and the western part of *South Tisza Basin* represent the recharge area of the groundwater flow regime where the chemistry of the water is controlled by *dissolution of calcite and dolomite* and by irreversible *solution of albite* in an open system. The other controlling factor is the Na *ion exchange* for Ca and Mg on clay minerals. The ion exchange came to equilibrium with the present composition of groundwater, the clay minerals contain Ca and Mg exchangeable cations (Varsányi, 1989a,b, 1991, Varsányi and Ó.Kovács, 1997). Two boreholes reviewed in this paper, *Kecskemét-1* and *Csongrád-1* are close to the northern boundary of this area. *Chloritic interlayers* in the expandable structure (Fig. 6) may reflect the adsorption and fixation of Mg ions in the interlayer space. High detrital calcite, dolomite and feldspar contents provide sufficient material for dissolution. Calcites and dolomites in the *Kecskemét-1* borehole proved to have nearly ideal stoichiometric composition by X-ray analysis.

The *Maros alluvial fan* is a similar flowing groundwater system, in a similar geological setting (Varsányi, 1989a,b). This is reflected in the similar character of the clay mineral assemblage. Flow direction is from SE to NW. The recharge area is mostly beyond the state borders. The wells *Kevermes-II/P* and *Tótkomlós-III/P* are situated closer to the recharge area and the well *Pusztaottlaka-I/P* closer to the discharge area. The main chemical reaction that may be expected according to the hydrogeochemical calculations, is *ion exchange.* This can be probably related to the Na-smectite contents of the *Kevermes* samples and to the dominantly divalent exchangeable cations in the *Pusztaottlaka* samples. *Chloritic interlayers* in the mixed-layer structure occur in all three wells, at *Pusztaottlaka* only in the upper few hundred metres. Low carbonate contents and carbonate concretions may indicate *dissolution and later precipitation of carbonates* from the flowing groundwater.

Contrary to the previous two flow systems the *Körös Basin* is a *discharge area.* The aquifer is filled either with stagnant, or very slowly upward flowing water. The boreholes *Dévaványa-1* and *Vésztő-1* are situated in the central part of the Quaternary basin. According to hydrogeochemical calculations dissolution of calcite and dolomite resulted in *equilibrium* between solids and water in relation of the ions Ca and Mg in lower levels while *oversaturation and precipitation* of carbonates occurs in the upper zones. The mineralogical record shows extremely little average carbonate contents and occasionally carbonate concretions of non-ideal calcite composition. This is probably partly due to dissolution and precipitation by the groundwater. On the other hand, no equlibrium composition in respect to silicate minerals was achieved according to the calculations and additional *dissolution of albite* proceeded in upper levels. In the <2 μm fraction of *Dévaványa* samples there are 14 Å smectite, kaolinite and mixed-layer kaolinite/smectite as well (Fig. 7). The product of albite dissolution may be *kaolinite* and not only *smectite* as it was supposed by Varsányi and Ó.Kovács (2001) and Varsányi (2001).

Hydrochemical data show decrease of Na contents in the upper 300 m zone of the Körös Basin. Accordingly adsorption of Na on clay minerals was supposed by Varsányi (2000). This does not appear on the smectites studied. Both in the boreholes *Dévaványa-1* and *Vésztő 1* the d values of the 001 basal reflection are at 14 Å, both in the bulk rock and in the <2 μm fraction, invariably in the whole depth interval of 0 to 1000 m.

Because of the upward flow of Lower Pannonian waters there is no strict boundary between the Lower Pannonian and Upper Pannonian water regimes in the Körös Basin. According to Varsányi (2000, 2001) the effect of the upward flowing Lower Pannonian water can be traced up to 1000 m depth. It is interesting that this boundary coincides with the change of the clay mineral composition (less smectite, more kaolinite) in the lowermost part of the *Dévaványa-1* bore hole.

A remarkable conclusion of the geochemical calculations discussed so far is that in the groundwater flow regime comprising the Pliocene and Pleistocene, *reactions involving* potassium do not play any role. On the other hand, according to investigations of Eberl (1993) in the Gulf Coast area the charge of the smectite layers may be increased by substitutions in the silicate layer and K^+ ions may be accumulated in interlayer sites of the high-charge smectite in shallow levels, at temperatures below cca. 80 °C. Potassium can be enriched in the formation water by dissolution of the K-bearing minerals K-feldspar and mica. All that leads only to slight gradual decrease of the smectite proportion in the mixed-layer structure from about 80 % to 60 %, but this is the first important step in the smectite to illite transition.

Data on the composition of *mixed-layer illite/smectites* published by Viczián (1992) and by Tanács and Viczián (1995) from 10 bore holes show that similar processes proceeded also in the Great Hungarian Plain *roughly above the Lower/Upper Pannonian boundary*. The boundary does not sharply coincide with the lithostratigraphic boundary, in the same manner as also water regimes may communicate across the boundary in the *Körös Basin*. Data of the papers cited and of the present review show, that variable composition is typical feature of the mixed-layer illite/smectites occurring above the Lower Pannonian. The composition is variable within a single sample and it varies also with the subsurface depth. The average smectite proportion of the samples drops with increasing depth from S=80-100 % to 30-50 %. In Lower Pannonian and older Neogene sediments illite/smectites are rather uniform within a single sample and generally low smectite proportions occur (S=10-50 %).

These data show that the *first main phase* of the smectite to illite diagenetic transition proceeds above the Lower/Upper Pannonian lithostratigraphic boundary, but below the Pliocene. What is left, is the *Upper Pannonian* (Upper Miocene, Újfalu and Zagyva Formations, "Pontian"). The water-rock interaction in this lithostratigraphic horizon is not yet well known, but mineralogical data show that dissolution of potassium minerals and fixation of potassium ions in the smectitic layers may proceed in this zone. Simultaneously, the same "Pontian" layers are considered by Varsányi et al. (1997) as "the main zone of kerogen diagenesis", in which the reactions resulting in kerogen formation, polymerisation and polycondensation are going on.

CONCLUSIONS

1. There is a wealth of mineralogical data on the composition of alluvial sediments of the Great Hungarian Plain (Alföld). The composition is basically the same in the whole basin: a *polymineralic detrital* clay mineral suite displaying slight systematic regional differences. There is no significant difference between the composition of various stratigraphic horizons in the time interval Upper Pannonian – Upper Pliocene – Pleistocene. Neither the clay mineral relations, nor the quartz to feldspar ratio differ significantly (Tables 1 and 2, Figs. 2, 3 and 4). This is especially interesting because it shows that the composition of sediments was practically independent from the highly varying climatic conditions. On the other hand, sub-basins differ from each other for long periods of time which is the result of the different source areas and shows the importance of the palaeo-tectonic setting.

1.1. The limited number of data from the Jászság Basin indicate higher *smectite* contents which is probably the effect of the northern volcanic areas.

1.2. The most "fresh" material, consisting of *illite* and *chlorite* and of many detrital non-clay minerals, such as *carbonates* and *feldspars* came from the ancient Danube into the Danube-Tisza Interfluve area and South Tisza Basin.

1.3. The composition of the Maros River Alluvial Fan is similar to the sediments derived from the Palaeo-Danube, but it contains *less carbonate*. Among the clay minerals there is much *smectite+illite/smectite* and a little *kaolinite*.

1.4. Sediments of the Körös Basin have the most mature composition, they are almost *carbonate-free*. Clay minerals are less well crystallised, disordered. Typical phases are *disordered kaolinite*, *mixed-layer kaolinite/smectite* and *iron hydroxides* (from *amorphous phases* to *goethite*). The dominant expanding phase of the <2 μm fraction is here discrete *smectite* while in other basins *mixed-layer illite/smectites* are more frequent.

2. Correlation may be found between variation of chemical composition of groundwater flow regimes and mineralogy of enclosing sediments.

2.1. In the Pleistocene and Pliocene horizons of the South Tisza Basin and Maros Alluvial Fan water flow regimes may cause dissolution of carbonate minerals and albite and ion exchange on clay minerals. Secondary carbonate concretions and neoformed clay minerals may be precipitated. *Ion exchange for magnesium* and subsequent fixation in the interlayer space may produce *chloritic interlayers* in mixed-layer illite/smectites. However, decrease of smectite proportions in mixed-layers in this zone may be related to *palaeopedological illitisation* rather than to diagenetic reactions.

2.2. In the Pleistocene and Pliocene horizons of the Körös Basin interaction of albite with the very slowly upward flowing water regime causes neoformation of *pure smectite* and *kaolinite,* however no chloritic interlayers were formed in this sub-basin.

3. The first phase of diagenetic illitisation involving reactions with *potassium-bearing* minerals coincides well with the water flow regime developed in the Upper Pannonian sediments. In this zone *smectite proportions* drop to 30-50 % with increasing depth, however, wide compositional ranges are typical throughout the zone.

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